

The seven-membered nickelacycle [NiBr{o-CH=C(CF₃)C₆H₄CH₂PPh₂- κ²C,P}]{PPh(CH₂Ph)₂}

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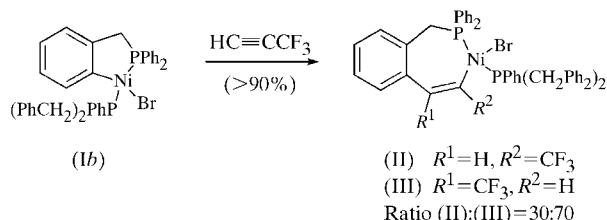
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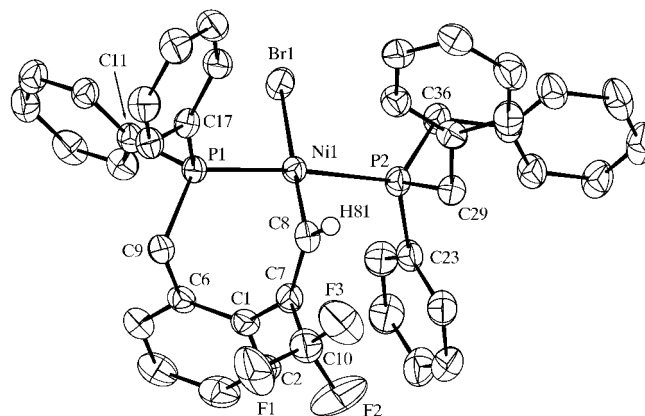
The crystal and molecular structures of the title compound, 3-bromo-3-(dibenzylphenylphosphonio)-2,2-diphenyl-5-trifluoromethyl-1*H*-benzo[*e*][1,2]phosphanickelacyclopentene, [NiBr(C₂₂H₁₇F₃P)(C₂₀H₁₉P)], which was obtained as the major regioisomer from insertion of HCCCF₃ into the Ni–C bond of the five-membered phosphanickelacycle [NiBr(*o*-C₆H₄CH₂-PPh₂-κ²C,P){PPh(CH₂Ph)₂}], have been determined. Principal geometric data include the Ni–X bond lengths Ni–Br 2.3343 (4) Å, Ni–P 2.1867 (7) and 2.2094 (7) Å, and Ni–C 1.882 (3) Å, and the two *trans* angles P–Ni–P 171.55 (3)° and Br–Ni–C 176.88 (9)°.

Comment

The insertion reactions of unsymmetrical alkynes with metallacycles have widespread applications in organic synthesis, but the origins of the observed regioselectivities are still unclear (Heck *et al.*, 1990; Abad, 1997; Spencer & Pfeffer, 1998; Cacchi, 1999; Cámpora *et al.*, 1999; Larock, 1999*a,b*; Bennett *et al.*, 2001). We have recently reported a systematic study of alkyne insertions into the Ni–C bond of the phosphanickelacycle [NiBr(*o*-C₆H₄CH₂PPh₂-κ²C,P)(PR₃)] [PR₃ = PEt₃ for (Ia) and PPh(CH₂Ph)₂ for (Ib)], in which electronic factors seem to play an important role in determining the geometry of the resulting seven-membered nickelacycles (Edwards *et al.*, 2001). This fact has since been supported by density functional theory (DFT) investigations of the insertion step for several alkynes with model



phosphanickelacycles (Macgregor & Wenger, 2002; Bennett *et al.*, 2001). This theoretical work includes the alkyne HCCCF₃,


Figure 1

The molecular structure of (III) with selected atom labelling. Displacement ellipsoids are drawn at the 50% probability level. With the exception of that on C8, H atoms have been omitted for clarity.

for which experimental data have only recently become available. The title compound, (III), was isolated as the major product from insertion of HCCCF₃ into the Ni–C bond of (Ib) (see *Scheme*), and a study of its structure was undertaken in order to establish its three-dimensional structure and mainly to confirm the location of the CF₃ group on the β-vinyl C atom. The molecular geometry of (III) is shown in Fig. 1 and the principal geometric parameters are given in Table 1. The Ni atom in the complex is in a distorted square-planar environment, with the two phosphine ligands *trans* with respect to one another. The seven-membered ring is in a boat-shaped configuration that renders the two phenyl rings of the cyclometallated PPh₂ group and the two benzyl groups of the auxiliary phosphine separately inequivalent.

Similar geometries have been observed for other related seven-membered phosphanickelacycles (Müller *et al.*, 1993; Edwards *et al.*, 2001), the carbocyclic species [Ni{C(CO₂Me)=C(CO₂Me)C₁₀H₆CF₂CF₂-κ²C,C}(dcpe)] [dcpe is bis-(dicyclohexylphosphinoethane)], which was produced by insertion of DMAD (dimethyl acetylenedicarboxylate) into the Ni–naphthyl bond of [Ni(C₁₀H₆CF₂CF₂-κ²C,C)(dcpe)] (Bennett *et al.*, 1995), and the carboxylate complex resulting from insertion of CO₂ into the Ni–phenyl bond of the nickelacycle [Ni(*o*-C₆H₄CMe₂CH₂-κ²C,C)(PMe₃)₂] (Carmona *et al.*, 1986, 1989). The bond lengths are unexceptional. The distances of the nickel–vinyl unit [Ni–C8 1.882 (3) Å and C7–C8 1.342 (4) Å] are similar to those reported for analogous compounds (Edwards *et al.*, 2001).

Experimental

The diffusion of HCCCF₃ into a solution of (Ib) in CH₂Cl₂ gave a very unstable mixture of the two isomeric insertion products [NiBr(*o*-C(CF₃)=CHC₆H₄CH₂PPh₂-κC,P)]{PPh(CH₂Ph)₂}, (II), and [NiBr(*o*-CH=C(CF₃)C₆H₄CH₂PPh₂-κC,P)]{PPh(CH₂Ph)₂}, (III) (spectroscopic ratio 1:2.5; yield > 90%). Attempted crystallization by diffusing pentane into a toluene solution of the mixture led to complete decomposition of (II), most likely due to β-hydride elimination, but orange single crystals of (III) could be isolated. ¹H NMR (300 MHz,

CD₂Cl₂): δ 3.06–3.30 (*m*, 4H, CH₂P), 3.54 (*dd*, 1H, *J* = 12.3, 8.7 Hz, CH₂P), 3.70 (*dd*, 1H, *J* = 14.4, 7.2 Hz, CH₂P), 6.70 (*br d*, 1H, *J* = 6.6 Hz), 6.99 (*d*, 2H, *J* = 6.9 Hz), 7.10–7.68 (*m*, 25H), 8.11 (*ddd*, 2H, *J* = 9.6, 7.8, 1.5 Hz); ¹⁹F NMR (188.2 MHz, C₆D₆): δ –63.7 (*app. t*, ²J_{PF} = 5.8 Hz, CF₃); ³¹P{¹H} NMR (81.0 MHz, CD₂Cl₂): δ 10.1 (*dq*, ²J_{PP} = 305.2, ⁴J_{PF} = 5.3 Hz, PPhBz₂), 36.5 (*dq*, ²J_{PP} = 305.2, ⁴J_{PF} = 5.7 Hz, PPh₂).

Crystal data

[NiBr(C₂₂H₁₇F₃P)(C₂₀H₁₉P)]
M_r = 798.28
 Monoclinic, *P*2₁/*c*
a = 18.3307 (2) Å
b = 10.9887 (1) Å
c = 18.7279 (2) Å
 β = 106.1717 (7)°
V = 3623.10 (6) Å³
Z = 4
D_x = 1.463 Mg m^{–3}
 Mo *K* α radiation
 Cell parameters from 58 628 reflections
 θ = 2.9–27.5°
 μ = 1.77 mm^{–1}
T = 200 K
 Prism, orange
 0.24 × 0.21 × 0.12 mm

Data collection

KappaCCD diffractometer
 φ and ω scans
 Absorption correction: Gaussian integration (Coppens, 1970)
T_{min} = 0.668, *T_{max}* = 0.831
 71 633 measured reflections
 8294 independent reflections
 5217 reflections with *I* > 3 σ (*I*)
R_{int} = 0.075
 θ_{max} = 27.5°
h = –23 → 23
k = –13 → 14
l = –24 → 24

Refinement

Refinement on *F*²
R = 0.031
wR = 0.036
S = 1.05
 5217 reflections
 447 parameters
 H atoms treated by a mixture of independent and constrained refinement
 Weighting scheme: Chebyshev polynomial with 3 parameters (Carruthers & Watkin, 1979): 0.650, 0.286 and 0.339
 $(\Delta/\sigma)_{max}$ = 0.001
 $\Delta\rho_{max}$ = 0.73 e Å^{–3}
 $\Delta\rho_{min}$ = –0.54 e Å^{–3}
 Extinction correction: Larson (1970)
 Extinction coefficient: 191 (18)

Table 1

Selected geometric parameters (Å, °).

Ni1–Br1	2.3343 (4)	P2–C36	1.852 (3)
Ni1–P1	2.1867 (7)	C1–C2	1.398 (4)
Ni1–P2	2.2094 (7)	C1–C6	1.403 (4)
Ni1–C8	1.882 (3)	C1–C7	1.491 (4)
P1–C9	1.844 (3)	C6–C9	1.511 (4)
P1–C11	1.829 (3)	C7–C8	1.342 (4)
P1–C17	1.813 (3)	C7–C10	1.487 (4)
P2–C23	1.838 (3)	C8–H81	0.90 (3)
P2–C29	1.821 (3)		
Br1–Ni1–P1	93.69 (2)	P2–Ni1–C8	85.00 (8)
Br1–Ni1–P2	94.70 (2)	Ni1–P1–C9	114.61 (9)
P1–Ni1–P2	171.55 (3)	C6–C1–C7	118.3 (2)
Br1–Ni1–C8	176.88 (9)	C1–C7–C8	123.3 (3)
P1–Ni1–C8	86.57 (8)	Ni1–C8–C7	128.2 (2)

H atoms were placed in geometrically determined positions and their coordinates were allowed to ride on those of the attached C atoms (C–H = 1.00 Å), with the exception of the vinylic H atom, for

which positional and isotropic displacement parameters were included in the refinement.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS* and *maXus* (Mackay *et al.*, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1096). Services for accessing these data are described at the back of the journal.

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